

HEYROVSKY, Jaroslav. 1890 - ed.

Collection des travaux chimiques de Tsecoslovaquie;
Collection of Czech. chem. communications . . . annee 1
Prague, 1929 - Edited and published 1929 by E. Votacek
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scientiarum bohemia. Published monthly with the aid of
the Board of Education of the Czechoslovakian Republic.
Vol. 1 includes section "Bibliography of Czechoslovakian
chemical publications."

HEYROVSKY, Jaroslav 1900 -

The deposition of radium and other alkaline earth metals at the dropping-mercury cathode. J. Heyrovsky and S. Berezicky. Charles Univ., Prague.
Collection Czechoslov. Chem. Comm. 1, 19-45 (1929)

Received 2 July 1929, 123, 810, 1237

HEYROVSKY, Jaroslav 1890 -

Electrolysis with mercury cathode. II. Explanation of the anomalies on the electro-capillary curves. J. Heyrovsky and R. Simunek. Phil. Mag. (7), 7, 951-70 (1929)

HEYROVSKY, Jaroslav 1900 -

Maxima on current-voltage curves. III. The electrolysis of mercury salt solutions with dropping and steady mercury cathods. P. Hrasymenko and J. Heyrovsky and K. Tancakivsky. Trans. Faraday Soc. 25, 152-9 (1929)

HEYROVSKY, Jaroslav 1890 -

A study of some complexes by the polarographic method. M. N. Demassieux
and J. Heyrovsky. Bull. soc. chim. 45, 30-5 (1929)

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Electrographic studies with the dropping-mercury cathode. XV. Positive and negative maxima on current-voltage curves. J. HRYNIOVSKY AND M. DUBINSKY (Collection Czechoslov. Chem. Comm. 2, 1031, 34(1936)). The anomalies observable on electrocapillary curves obtained by the drop wt. method have been shown (C. A. 24, 2975) to be indicated on the current voltage curves by prominent max. which are given under conditions of imperfect polarization of the dropping Hg cathode. Theoretical treatment of these anomalies is given in the present paper, and it is shown that the presence in soln. of a highly adsorbable substance, e. g., an org. dye, prevents this imperfect polarization and, therefore, the anomalous shape of the current voltage curve. The max. occurring on current voltage curves when solns. contg. electro-reducible substances are electrolyzed with the dropping Hg cathode are termed "positive" or "negative" according as they are given at potentials more pos. or more neg. than the a/c. electrocapillary zero (i. e., 0.56 v. from the N calomel a/c.). The shape of the electrocapillary curve, simultaneously derived from the polarized dropping Hg cathode, indicates the sign of the max. Just as the pos. branch of the electrocapillary curve is affected by the presence of adsorbable anions, and the neg. branch by adsorbable cations, the presence of such anions has been shown to affect the pos. max., while neg. max. have been shown to be sensitive to cations. The current voltage

curves were obtained in the usual manner (C. A. 19, 2965), and the electrocapillary curves by catching and weighing 50 drops of Hg (from the dropping cathode) at various applied e. m. fs. Adsorbable, or multivalent anions, such as CN^- , OH^- and SO_3^{--} and acidic dyes and neg. coloids, suppress pos. max., leaving the neg. ones unaffected, while multivalent cations, even in dil. soln., suppress neg. max. and are without effect on pos. ones. The degree of suppression of pos. max. given by the OH^- and that by the SO_3^- ion are identical at equiv. concns., while that of the NO_3^- ion is much less. This is exactly parallel to their respective effectiveness in the pptn. of $Fe(OH)_3$ soln.

EDWARD H. SAMUELS

ASB 33 A METALLURGICAL LITERATURE CLASSIFICATION

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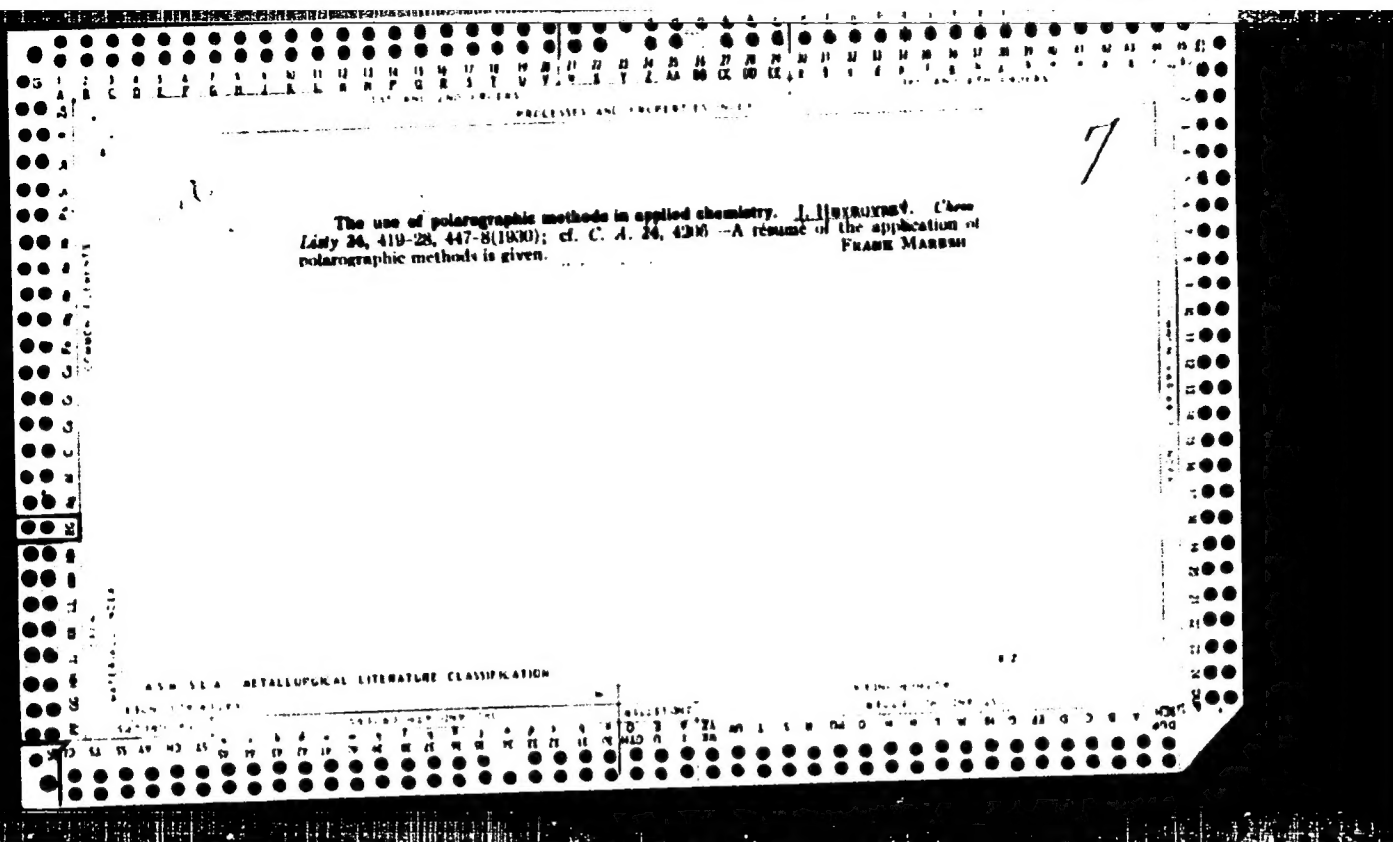
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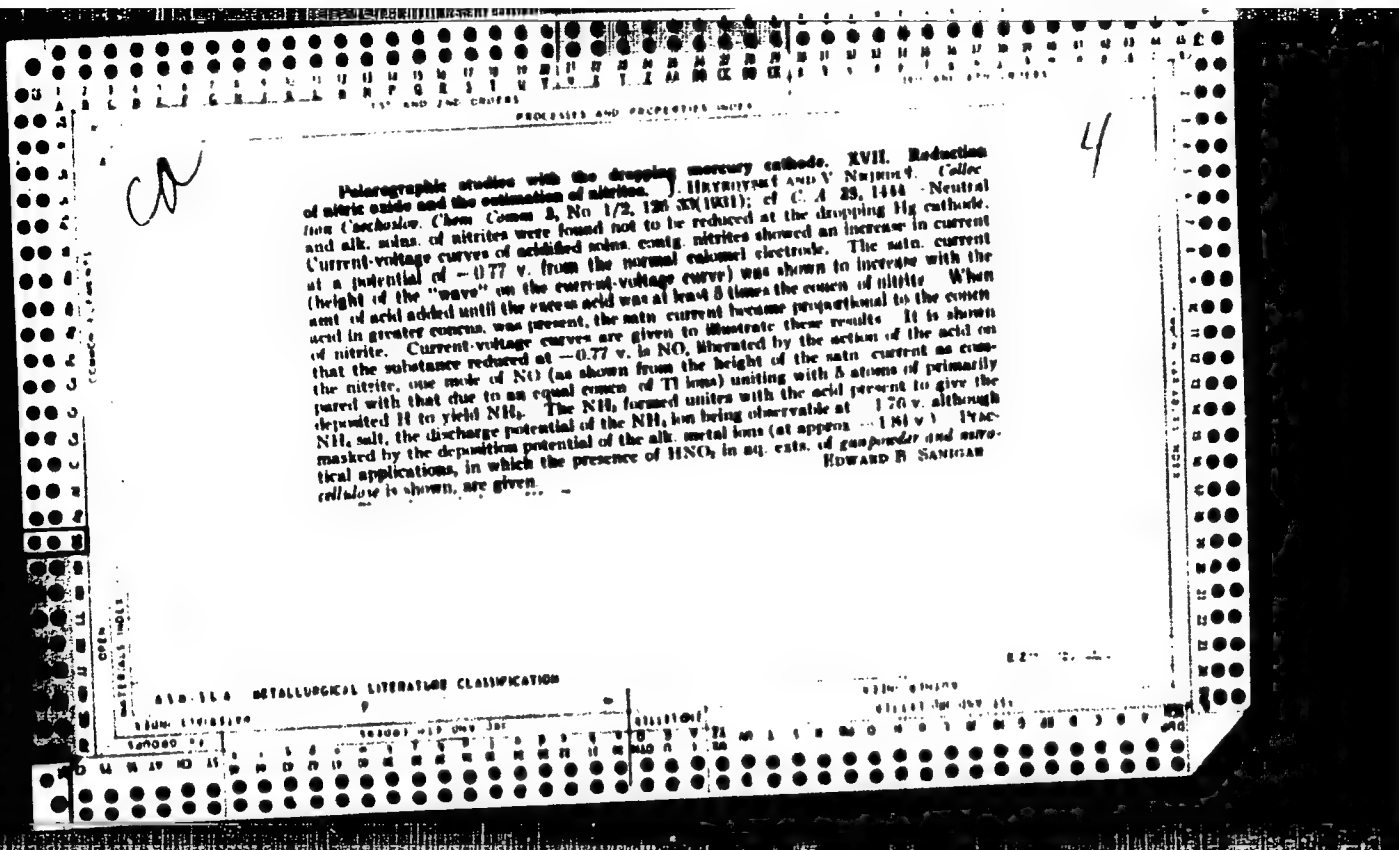
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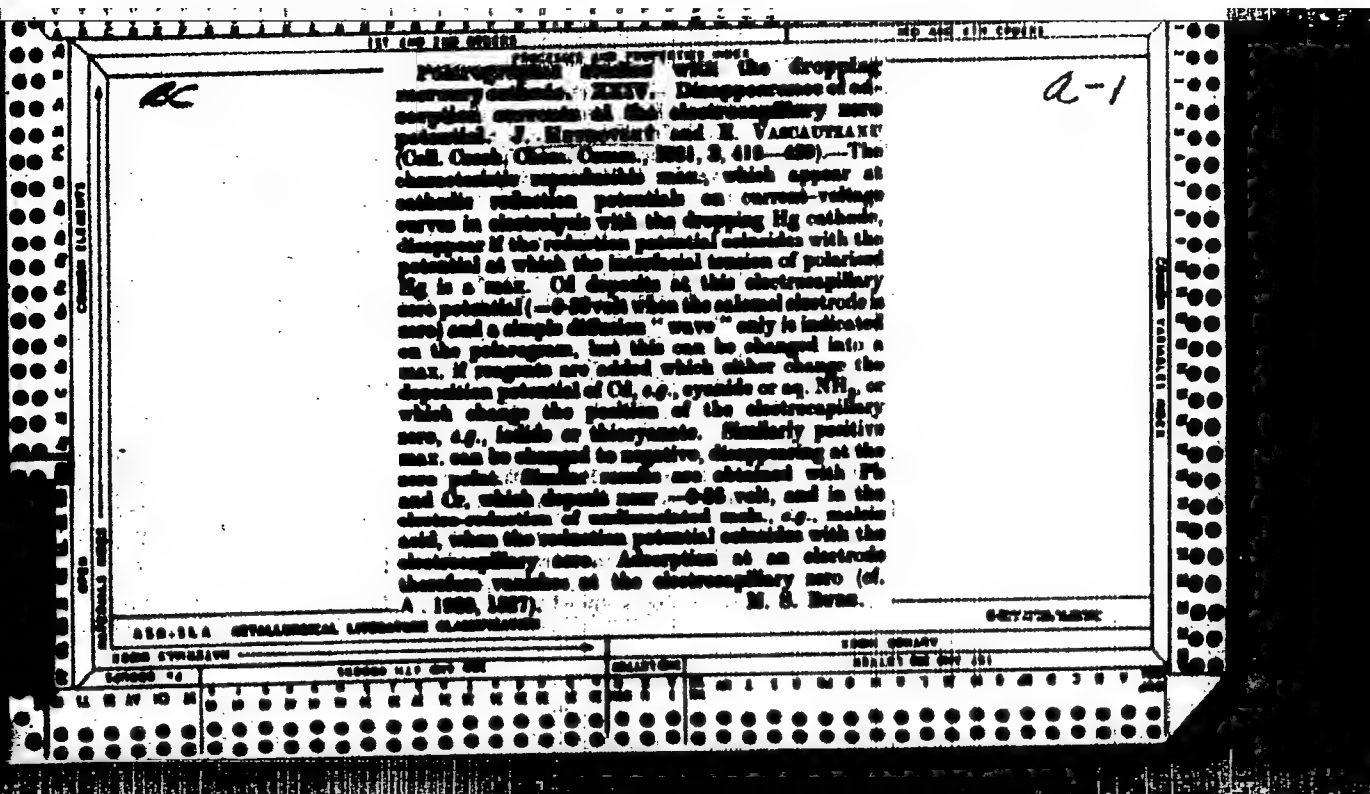
HEYROVSKY, Jaroslav 1390 -

_____ and J. Babicka: P.S.D.M. Kathode. The effect of proteins.
Chem. News 141, 369 and 385 (1930)

COMMON ELEMENTS										PROCESSES AND PROPERTIES INDEX									
<p>2A</p> <p>Polarographic examination of vinegar with the dropping-mercury cathode. J. HEVROVSKI, L. SHOLAR AND J. STASTNY. <i>Vestník Českoslov. Akad. Zemedelství</i> 6: 490-500(1960); cf. C. A. 24, 3650. — Reproducible results are automatically recorded. Fermentation vinegar contains AcH, as intermediate product of bacterial alc. fermentation, and surface-active substances. B. C. A.</p>										<p>15</p>									
<p>ASM-11.6 METALLURGICAL LITERATURE CLASSIFICATION</p>										<p>FROM SOURCE</p>									
<p>100000 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100</p>										<p>100000 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100</p>									







Estimation of oxygen by the polarographic method. J. HRYMONET. *Ann. Chim. Phys.* 5, 162-71 (171-3 English) (1931).—Current-voltage curves obtained in electrolysis with the dropping Hg cathode and a large Hg anode are strictly reproducible and permit qual. as well as quant. conclusions on electro-reducible substances present in the electrolyzed soln. The method is very convenient if automatic recording of current-voltage curves is made photographically by a polarograph. The curves obtained from solns. electrolyzed when exposed to air always show two summits (two "waves") which are due to the reduction of O to H_2O_2 and then to H_2O . When 0.3% H_2O_2 is dropped into 20 cc. 0.1 M salicylic acid an increase in the 2nd wave can be seen. In this way H_2O_2 and all peroxides can be detd. In alk. solns., however, H_2O_2 is unstable, decaying to O. Curves are given for various expts. One curve serves as an example of quant. estn. of O in tech. gases. The sensitivity of the method is such that 0.2% O in gases or 0.1 ml. per l. of soln. may be estd. with 5% accuracy, 1 cc. of the soln. being sufficient for analysis and the curve being obtained in 5 min. In one figure a decrease of O is shown by curves to the soln. in which plants are decaying. The method is reliable only in the absence of oxidizing agents and ions of nobler metals, which may be easily removed by alkali hydroxides. J. KUCERA

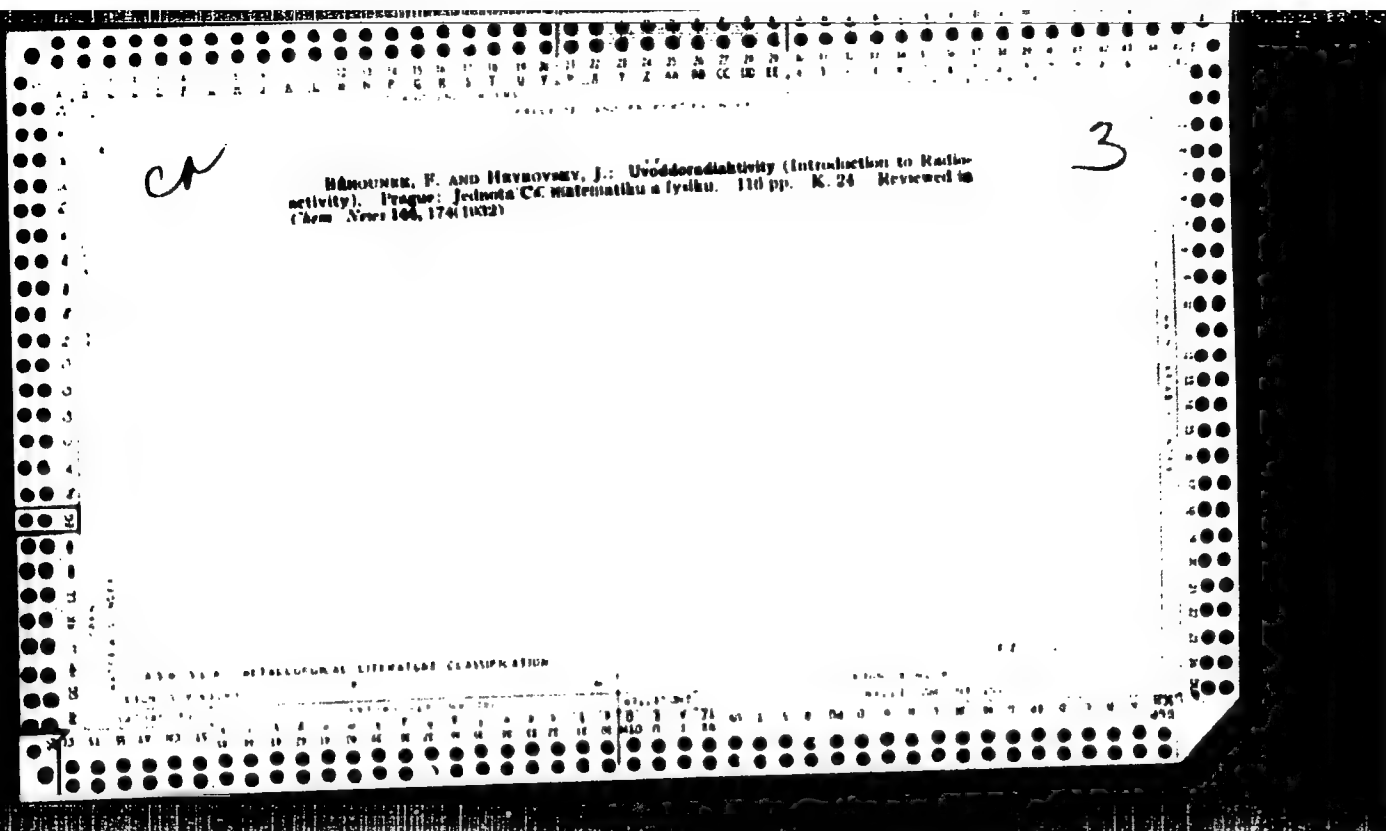
HEYROVSKY, Jaroslav 1900 -

Analysis of petroleum and its distillates for reducible substances and the adsorbable matter by means of the polarographic method with the dropping-mercury cathode. E. Gorman and J. Heyrovsky. Trans Electrochem. Soc. 59 (preprint), 23 pp. (1931) - pp. 249-271

Also appears in J. Amer. Electrochem. Soc. 27, IV (1931)

HEYROVSKY, Jaroslav 1931 -

_____ and V. Nejedly. The electroreduction of nitric oxide and the estimation of nitrites at the dropping mercury cathode. Chem. News 142, 193-97 (1931)



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Polarographic studies with the dropping-Hg cathode. XXX. Electroreduction and estimation of fructose and sorbose. J. Heyrovský and I. Šmolík. *Collection Czechoslov. Chem. Communications* 4, 621-30 (1932) in English, cf. C. A. 21, 1917, 2905, 25, 1740; 27, 708. — The inversion of sucrose was quantitatively followed polarographically. The velocity const. was not strictly linearly proportional to the pH , but increased more than was expected from the increase in acidity. The electroreduction potentials of fructose and sorbose in neutral or weakly alk. solns are given as 1.8 v. The shift in the reduction potential of fructose with diln. is abnormally large, the values being 1.57 v. for 0.01 M soln. and 1.66 v. for 0.001 M soln. It is concluded from the large temp. coeff. of the diffusion current due to the reduction of ketoses that they exist in soln. in two tautomeric forms, only one of which is electroreducible. F. B. S.

ASAC-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA 7

Application of the polarographic method to micro-analytical work. J. HAYROVANT.
Mikrochemie 12, 26 (1932); cf. C. A. 25, 2050. --The polarographic method depends upon the automatic registration of strictly reproducible p.d. curves obtained during the electrolysis of a small portion of soln. with a slowly dropping Hg cathode and a large Hg anode. The necessary app. is shown and described. Numerous polarographic charts are shown and a bibliography is given of pertinent literature. Almost all cations except Ag, Hg, Au, Mg and Ta can be detd. in this way. Their oxidation potentials as well as those of some 50 org. compds. are given, all of which can be detected by the method. W. T. H.

ASD-510 DETALLUPICAL LITERATURE CLASSIFICATION

HEYROVSKY, Jaroslav 1300 -

Der Polarograph und seine Anwendung (tschech., 4 S.
Elektrotechnicky obzor 21, 37 (1932).'

PROCESSES AND PROPERTIES INDEX

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The reduction of fructose by the mercury drop cathode and the determination of invertase by the polarographic method. *J. Stevanović and I. Stanić. Chem. Listy 56, 479-84(1932).*—The ketones fructose and sucrose were reduced by the Hg drop cathode in neutral or slightly alk. solns. at a potential of -1.80 v. The polarographic curve shows a rise in the current which is directly proportional to the concn. of the ketone. The aldoses glucose, mannose, rhamnose, L-arabinose and lyxose and the alcohols

sucrose, maltose and lactose are not reduced by the cathode; their presence has no influence upon the course of the reduction of ketones. Fructose and invertase were detected in solns. of sucrose and honey with a precision of 2-10% in concns. of 0.001% of the ketones; 0.2 cc. of soln. sufficed for the detn. The easier reduction of the ketone rather than the aldose is ascribed to the presence of the large no. of acidic OH groups which influences the fundamental constitution and makes the ketone susceptible to electroreduction. Because of temp. changes during the reduction, abnormal deviations occur in the polarographic curve; definite conclusions about the current required for a g. mol of the reducing substance are not possible.

FRANK MARSH

ASB-55A METALLURGICAL LITERATURE CLASSIFICATION

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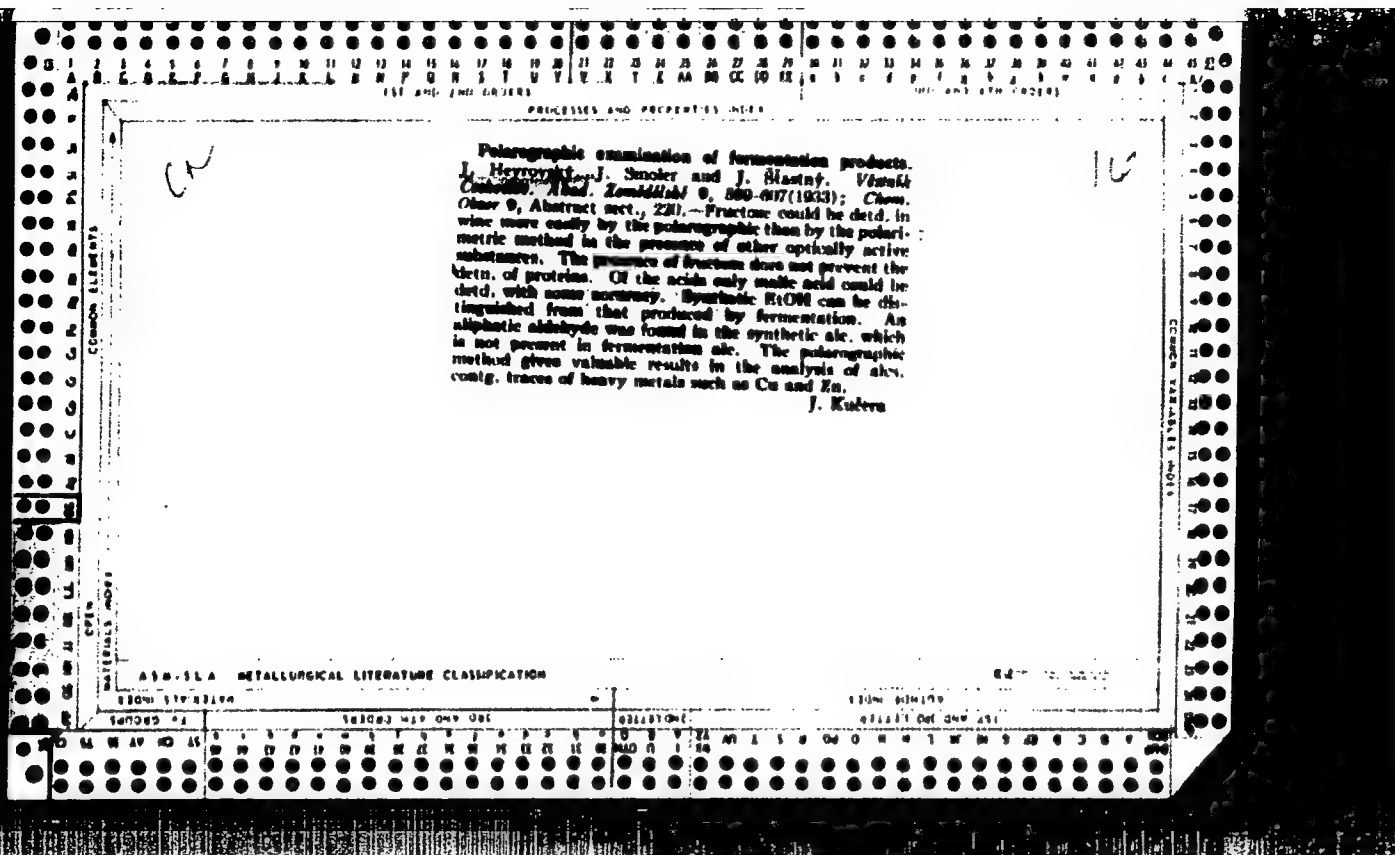
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Anwendung der polarographischen Methode in der praktischen Chemie (tschech.).
Prag: Institut der "Akademie der Arbeit", 1933



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Anwendung der polarographischen Methode in der praktischen Chemie (tscheck.).
Verlag Csl. svaz pro vyzkum a zkouseni technicky dulezitych latek a konstrukci.
Ustav Masarykovy akademie Prace (1933), No. 10, 124 S.

HEYTCHSKY, Jaroslav 1900 -

Industrial applications of the polarographic method of analysis.
Chimie & industrie, Special No., 204-10 (June 1933).

(Note: Another index lists this as Chimie & industrie, 29, No 6 bis,
204-211 (1933))

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Research Materials, (19...).

Referred to (19...), (March 10, 19...).

HEYROVSKY, Jaroslav 1990 -

Die Theorie der Wasserstoffueberspannung und ihrer katalytischen Herabsetzung an der tropfenden Quecksilberelektrode (russ.). Trudy jubileinogo Mendeleevskogo sjezda 1934, 305-309.

The theory of overpotential of hydrogen and its catalytic lowering at the dropping mercury cathode. Travaux du congres jubilaire Mendeleev, p. 299-303. Moscou, Leningrad: Edition de l'Academie des sciences de l'URSS, 1937.

HEYROVSKY, Jaroslav 1990 -

A polarographic study of the electro-kinetic phenomena of adsorption,
electro-reduction and overpotential displayed at the dropping mercury
cathod. Paris, Hermann et c^{ie}, 1934. Bibliog, n. 47-8
Actualites scientifiques et industrielles No 90.

Limiting currents in electr. cells with the dropping-mercury cathode. J. Heyrovsky, *Acta Hem. Farm.* 6, 11-16 (in English) 16 (1931). The limiting currents which are observed on current-voltage curves, recorded polarographically during electrolysis with the dropping-Hg cathode, are detd. by the rate of diffusion and migration of reducible ions. The ratio of the "diffusion" current, i_d , to the total limiting current, i_l , when the reducible electrolyte is present alone in the soln., is expressed by the equations $i_d/i_l = \nu/(n + \nu)$ and $i_d/i_l = (2\nu + n)/(\nu + n)$ for the reduction of cations and anions, resp. The addn. of an excess of an indifferent electrolyte transforms the limiting current into a pure "diffusion" one, since it stops migration by eliminating the drop of potential in the soln. The limiting current of the cations is thereby lowered to about $1/2$, whereas that of the anions is increased by about $1/2$. The drop of potential may be increased by introducing into the soln. a substance which is reduced at a smaller voltage, in this case the cationic limiting current is increased while the anionic current decreases. Limiting currents due to the reduction of nonelectrolytes are not influenced by the presence of salts. For quant. polarographic detns. in which concn. is measured in terms of limiting currents, an excess of indifferent electrolyte should always be added in order to obtain a pure "diffusion" current. The formulas given may be applied for detn. of transport nos. by measuring the "migration" and "diffusion" components of the limiting currents. J. Kučera

ASAC 3.1.1 DETAILING LITERATURE CLASSIFICATION

HEYROVSKY, Jaroslav 1320 -

Polarographische Untersuchungen von Mineralwaessern (tschech.). Vestnik
balneol. a klimatol. spol. 14, 83-94 (1934)

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17

Polarographic applications in pharmaceutical chemistry.
J. Heyrovsky. *Czechoslovak Laboratories* 10, 985-9
(1965). The polarographic method with the Hg drop
cathode can be used for microanalysis and especially for
the detection of impurities in chemically pure chemicals.
Cu, e. g., can be detd. by this method in such small amounts
as 0.005-0.0005%. In addition, this method can be applied
to the detn. of traces of heavy metals, bromate, iodide,
vinyl alc. In other, the purity of ether, of benzene and of
different sugars, formaldehyde, saccharin in sweetening
substances, some of the toxicity of arphenanthroline prepa-
rations of peroxide in triethyl (cf. Petrash, C. A. 27, 1714).
V. D. Karpenko

ASD-SLA METALLURGICAL LITERATURE CLASSIFICATION

1st and 2nd copies

PROCESSES AND PROPERTIES INDEX

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Professor Schuster Brunner, J. Heyrovsky, Collec-
tion Czechoslov. Chem. Communications 9, R2 (1965).
Obituary with portrait. R. H.

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Polarographic studies with the dropping-mercury cathode. XLVIII. Overpotential in heavy water. J. Heyrovsky and O. H. Müller. *Collection Czechoslov. Chem. Communications* 7, 281 (1942); cf. C. A. 39, 2659 (1944, 4678). Solns. of HCl and other electrolytes in 3 to 99.2% D₂O were investigated polarographically. The current-voltage curves were the same as for solns. in H₂O for the $b \log i$ term of the Tafel relation, oxidation of the current, lowering of overvoltage by quinone, deposition of alkali metals, reduction of atm. O, depolarization of OH ions or the electroreduction of D₂ (99.2% D₂O) is 20-25 mv. more neg. than for H₂ in H₂O for dil. HCl solns. Large

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differences in the shape of maximums due to secondary catalytic processes were noted. Two soln. cells contg. 0.1 and 0.5 cc., resp., were employed and the collection point of Ti was used for reference. XLIX. Electroreduction and estimation of bromates and iodates. A. Rylich. *Ibid.* 7, 289 (44).—The reduction potential of 0.001 N IO₃ and BrO₃⁻, resp., in 0.1 N soln. of electrolyte was (a) univalent cations (Na, K) -1.00 v., -1.00 v., (b) bivalent cations (Ca, Sr, Ba) -0.84 v., -1.31 v. and (c) trivalent cation (La) -0.40 v., -0.63 v. In acid soln. the values for IO₃⁻ and BrO₃⁻ were +0.13 v. and -0.10 v., resp. In the latter case the voltage change is abrupt and is explained as due to the formation of ion pairs of low dipole moments with H⁺. The reaction $IO_3^- + 6e + 3H_2O \rightarrow I^- + 6OH^-$ occurs in one stage. Reductions of ClO₃⁻ and ClO₂⁻ are not reproducible. The polarographic analytical estn. of IO₃⁻ in any excess of bromate or chlorate or of BrO₃⁻ in any excess of chlorate is sensitive to one p. p. m.; similarly traces of iodide in chloride can be detd. by conversion to iodate. IO₃⁻, BrO₃⁻, NO₃⁻ (NO₂⁻) can be simultaneously detd. R. E. DeRight

ASB 51.6 METALLURGICAL LITERATURE CLASSIFICATION

4

The catalytic deposition of hydrogen on the dropping mercury cathode. - J. Heymans, *Pittsburg* 28, 212 (1935); *Chem. Abs.* 13, Abstracts 105. - Before the decomposition potentials were reached, curves for the salts of Ru, Rh, Ir and Pt had a wavelike appearance. The height of the waves was proportional to the acidity of the soln. and to the salt concn. Metals which readily dissolve in Hg (Au, Ag, Cu, Pb) did not show this effect. H. studied the effect of quaternary alkaloids and of the 500 group of amino acids. Hg sulfide pptd. from a neutral perchlorate soln. gave the most sensitive tests for Hg in the KCl salts.

Frank Marsh

1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

BC

a-1

Significance of depolarization potentials deduced from the current-voltage curves in electrolysis with a dropping mercury electrode. J. Harnovant and D. Ilkovic (Chem. Listy, 1985, 29, 234-235).—Published data (this vol., 988) are discussed. R. T.

ASB-564 METALLURGICAL LITERATURE CLASSIFICATION

FROM LITERATURE

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HEYROVSKY, Jaroslav 1930 -

Ueberspannung des schweren Wasserstoffes an der tropfenden Quecksilberelektrode
(tschech., R.). Chem. Listy Vedu Prumysl 29, 295-300 (1935)

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A sensitive polarographic test for the absence of rhenium in mangamous salts.
Nature 135, 870-1 (1935) and cf. Nature, 137, 121 (Jan. 18, 1936)

also

Ein empfindlicher polarographischer Nachweis der Abwesenheit des Rheniums in
Mangansalzen (tschech., R.). 5 S. Rozpravy II tr. Ces. Akademie 45, No. 8
(1935) item Bull. int. Acad. Boheme 1935.

HEYROVSKY, Jaroslav 1930 -

Polarographie, in W. Boettger: "Physikalische Methoden der analytischen Chemie", part 2, 260-322. Leipzig: Akademische Verlagsgesellschaft, 1936.

and

Fortschritte der Polarographie, in same reference, part 3, 422-77 (1939)

137 APR 1968										PROCESS AND PROPERTIES INDEX										138 APR 1968									
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<p>Polarographic studies with the dropping mercury cathode. LVIII. Electro-reduction of dinitrogen and oxamic acid. J. BANERJEE and J. KUMAR. <i>Can. J. Chem. Comm.</i>, 1966, 4, 114-124.—In aq. solutions of NaOAc, C_2N_2 shows an increase of current when the potential of the dropping Hg cathode is -1.15 volt with respect to the NHE electrode; this is attributed to direct electro-reduction of C_2N_2. The second increase of current at -1.45 volt is probably due to electro-reduction of oxamic acid or its salt. As the age of the solution increases, the first polarographic "wave" diminishes and the second increases. C_2N_2 has no effect on current-voltage curves of alkaline solutions, and in neutral or slightly acid solutions the second "wave" develops slowly but does not appear in more acid solutions. The results are interpreted in terms of the hydrolysis of C_2N_2. 10^{-4}–10^{-5} g.-mol. per litre of C_2N_2 and oxamic acid can be detected polarographically. J. G. A. G.</p>																													
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PROCESSES AND PROPERTIES INDEX

Polarographic studies with dropping mercury cathode. LXXX. Increase of sensitivity in determination of alkali metals. J. MAXIMOV and M. DUBAI (Czech. Chem. Comm., 1955, 8, 444-444).—In presence of dissolved O_2 or other reducible non-electrolyte (e.g., benzophenone), the ionic migration current i is increased over the val. found in the absence of non-electrolyte by an amount which is independent of the concn. of alkali ions, but of concn. of non-electrolyte and of the ratio u/v of the ionic mobilities of the alkali and anion. The alkali concn. may be determined from the potential gradient, as measured by the displacement of the polarographic wave; the ratio $Na:K$ may be calc. from the val. of u/v . J. S. A.

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

SECTION 1: 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100

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SECTION 6: 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100

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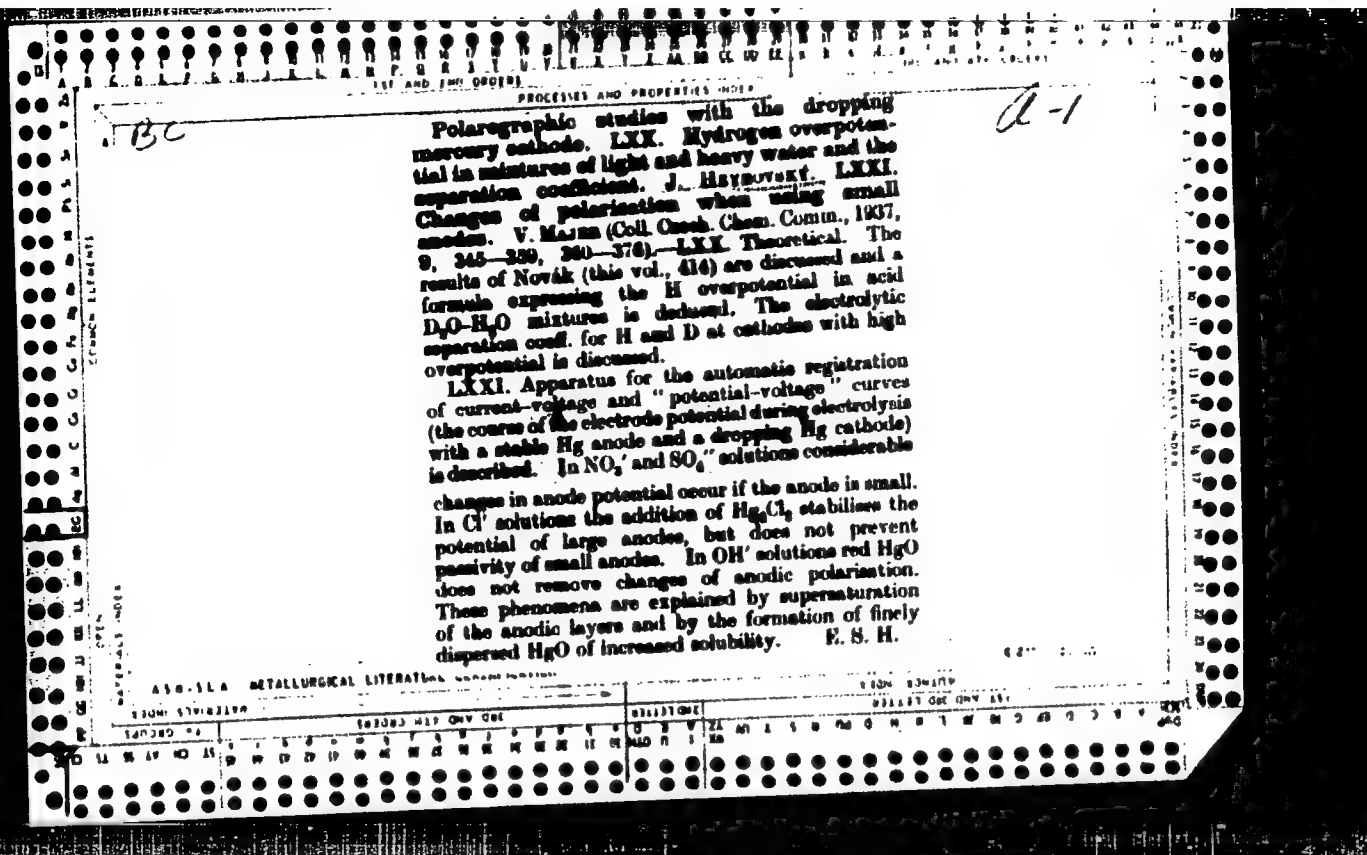
Die polarographische Methode, ihre Theorie und praktische Anwendungen (russ.,
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Theory of hydrogen overvoltage and its catalytic lowering at the dropping mercury cathode. J. Heyrovský. *Trans. conf. jubilee Mendeliev 2, 230-33* (1927). cf. C. A. 31, 6110⁹.—The lowering of H^+ overvoltage is attributed to increased adsorption of H^+ in the surface layer and to a catalytic effect in the metallic phase which brings about union of H atoms and H^+ . This may be a "metallic catalysis" brought about by metals of the Pt group, or a "solution catalysis" brought about by alkalis of the quinoline group or by certain compounds of the Sb group. B. C. A.

AS 0-110 METALLURGICAL LITERATURE CLASSIFICATION

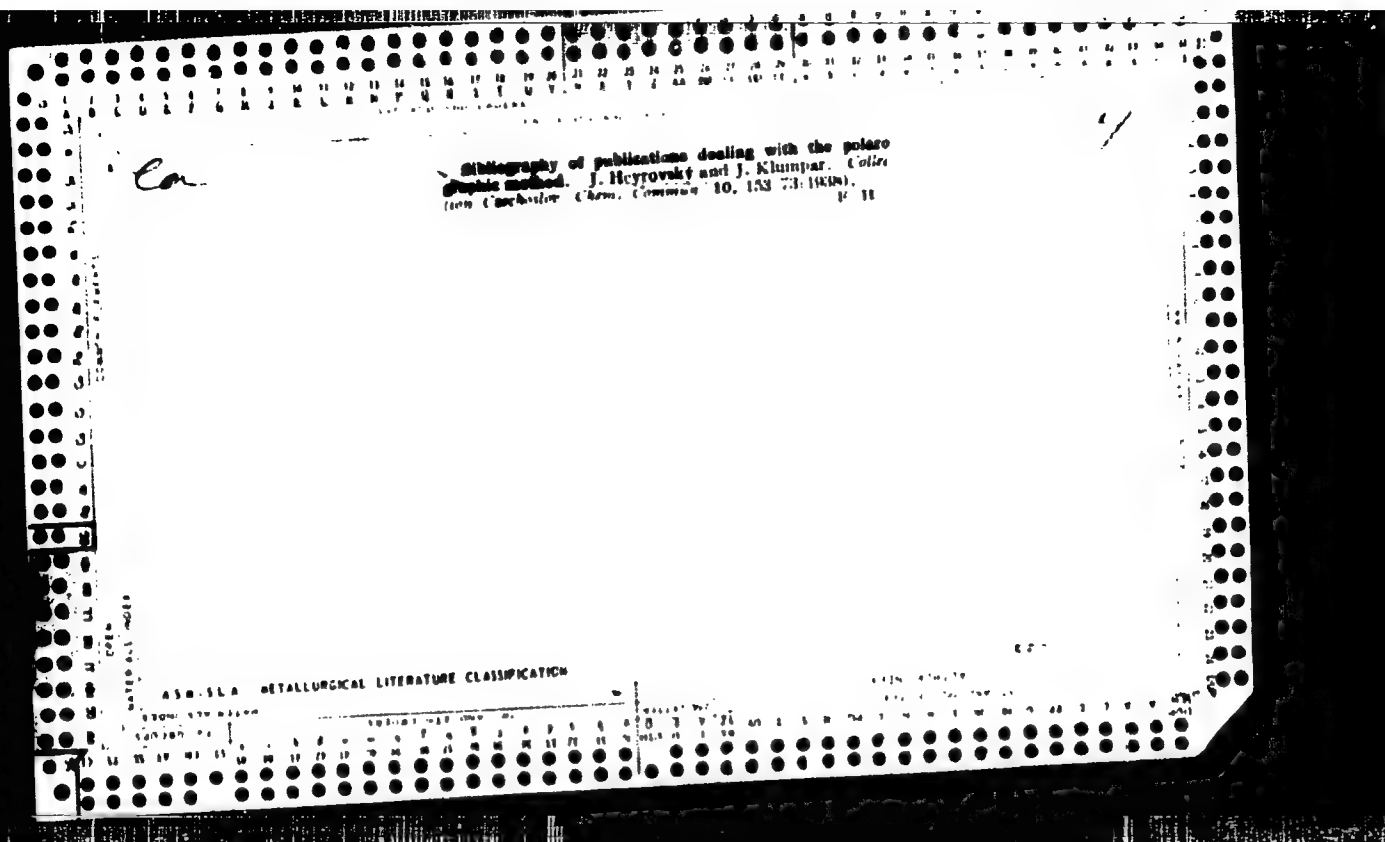
3. Polarographic studies with the dropping-mercury cathode. LXII. Hydrogen overvoltage in light and heavy water. A. Heyrovsky, *Collection Czechoslov. Chem. Commun.* 9, 273-301 (1947). Exptl. results of Novak et al. C. A. 31, 7764⁹ on the H_2 overvoltage at the dropping- Hg cathode in light and heavy water are interpreted theoretically by means of Heyrovsky's theory of overvoltage in terms of classical electrochemistry (C. A. 19, 1032⁹). The exptl. results contradict the idea that the heavy and light hydrions should be deposited at a different rate and all exptl. evidence agrees with the view that heavy and light hydrions are deposited indifferently and reversibly; also the solvation of H_2 proceeds by the union of the deposited H atoms with the hydrions of the solvent. The rate of the latter reaction is 5.4 times slower in D_2O than in H_2O since the ionic product and the rate of dissociation in D_2O are 5.4 times smaller than they are in H_2O . The same result is deduced in terms of the ionization constants of H_2O , HOD and D_2O , and the formula for the difference of overpotential in H_2O and D_2O is obtained. Heyrovsky's formula for overpotential is modified for large c , ds , by introducing the idea of adsorption of the H_2 moles at the interphase. The formula then agrees with exptl. curves. The theory explains why in D_2O the electroreduction of malic acid proceeds at a more pos. potential and the electroreduction of H_2O_2 at a more neg. potential than the same reactions in H_2O .

LXX. Hydro
gen overvoltage in mixtures of light and heavy water and
the separation coefficient (Ind. 345-50). Based on the
results of Novák (cf. A. 31, 2764) an equation for the
overvoltage of H in acidified mixt. of light and heavy
water is derived. The equation contains the mean ad-
sorption coeff. of the H mols. α , the mole fraction and
disconn. const. of H₂O, HDO and D₂O. Good agreement
between calcd. and observed quantities is obtained. The
electrolytic sepn. coeff. for the H isotopes at cathodes
with large overvoltage was formulated as dependent on the
compn. of the mixt. of light and heavy water and on the
c. d. The mean value is 5.4 which in concd. heavy
water should increase to 7.0 and in ordinary water decrease
to 2.7.



157 AND 158 CODES		PROCESSING AND PROPERTIES INDEX		300 AND 301 CODES	
<p><i>BC</i> <i>7-1</i></p> <p>Electrolytic reduction of dicyanogen, cyanic acid, and cyanide on a mercury dropping cathode. J. Boudry and J. ESTROVART (Chemp. Industriels, 1957, 17, 594-595). As current-voltage curves obtained in the electrolysis of freshly prepared CuCN solutions in excess of KCN show irregularities due to the formation of CuCN and free CN_2, the effect of CN_2 absorbed in neutral, slightly acidic, and alkaline solutions of various electrolytes is studied. CN_2 in NaOH causes an increase of current at the potential of the dropping Hg cathode -1.15 v. (vs. calomel = 0) due to the direct electro-reduction of the CN_2 gas absorbed, $(\text{CN}_2 + 2\text{O} \rightarrow 2\text{CN}^-)$ and another increase at -1.55 v. due to the electro-reduction of the amide product of hydrolysis of CN_2, probably $(\text{CO}-\text{NH}_2)$, $\text{NH}_2\text{CO}-\text{CO}-\text{H}$ or its salt, the mol. taking up 2 e. This supports the view that dicyan mon. with double linkages are adsorbable and electro-reducible at the dropping Hg cathode.</p> <p style="text-align: right;">F. R.</p>					
<p>ASD-158 METALLURGICAL LITERATURE CLASSIFICATION</p>					
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<p><i>bc</i></p> <p><i>A-1</i></p> <p>Overpotential of hydrogen at a mercury electrode in ordinary and heavy water. J. KATZ, <i>Adv. Chem. Ser.</i>, 1967, 34, 448-467. The reaction $H + D_2O \rightarrow HD + OD$ takes place at a Hg cathode. Since $[D^+][OD^-] = 0.185 \times 10^{-14}$ is $< [H^+][OH^-]$ all processes taking place at the cathode and involving interaction with water take place at a more negative potential in D_2O than in H_2O; to such processes belong the above, or the electro-reduction of aq. alkaline H_2O_2. On the other hand, processes involving only H or D proceed at the same rate; thus reduction of O_2, hydrogenation of fumaric or maleic acid, and deposition of cadmium occur at the same potential in D_2O and H_2O.</p> <p>R. T.</p>																									
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a Nancy 1938. Chim. et Ind. 35, 1043 - 1050 (1938)

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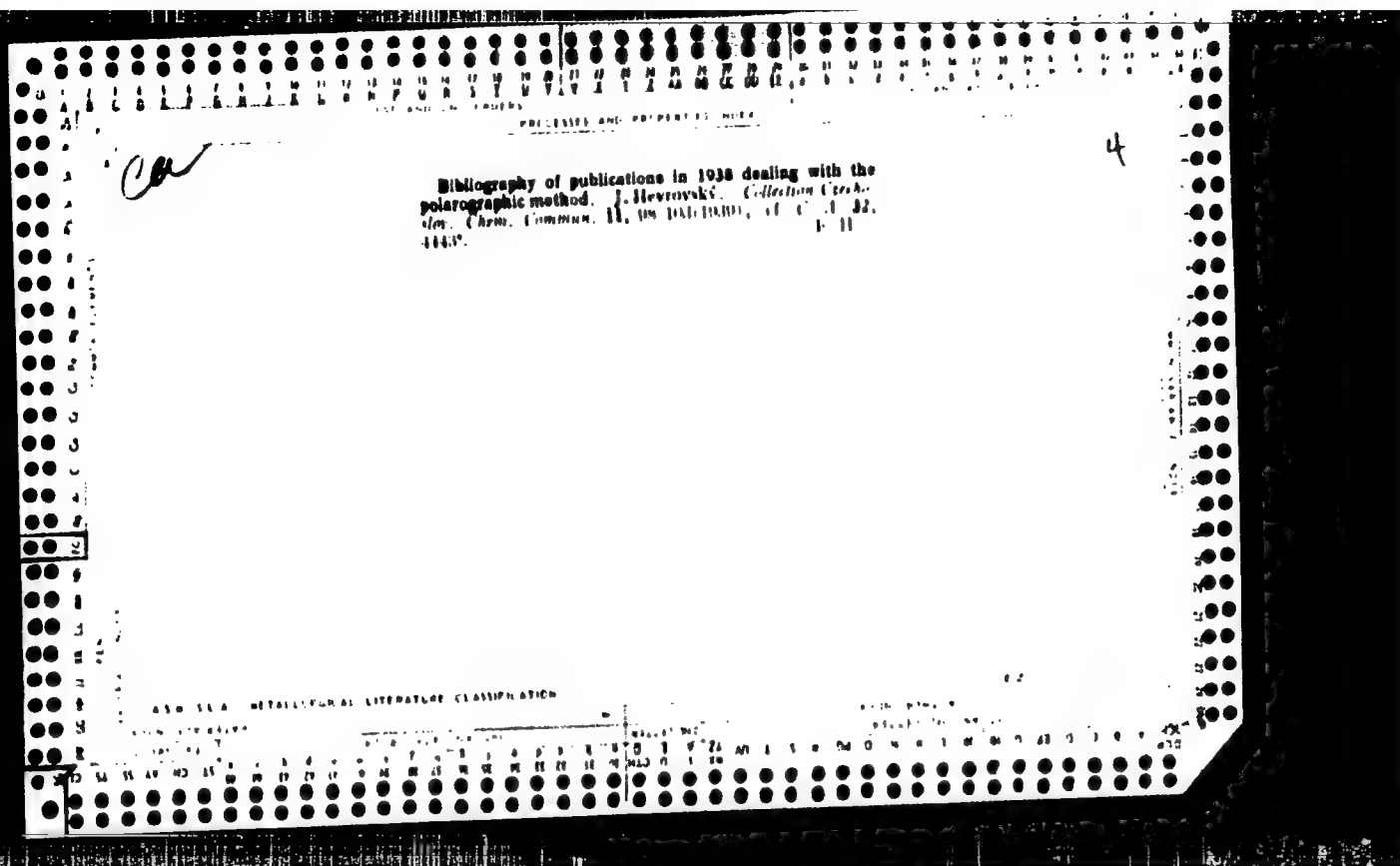
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TO: STP 11199
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DATE: 11-1-59

REMARKS: 11-1-59

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APPROVED FOR RELEASE: 08/10/2001

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1ST AND 2ND COPIES		3RD AND 4TH COPIES	
<p><i>Handwritten: 10</i></p> <p>A polarographic study of dilute amalgams. J. Heyrovsky and M. Kalousek. <i>Chem. Listy</i> 36, 47-51 (1940). Collection <i>Czech Chem. Commun.</i> 11, No. 11, 464-73 (1939).—Dil. amalgams contg. 0.005% Cu, Pb, Cd or Zn served as anodes for polarographic researches with the dropping Hg electrode. At critical voltages the metals dissolved in the Hg at the anode, entered the electrolyte and formed a current-voltage anodal wave upon the polarographic curve, of which the height depended on the concn of the metal in the amalgam and the position was characteristic for the metal entering the electrolyte. The potential of the anodal wave during the soln. of the metal in the electrolyte was given by the voltage when the diffusion current reached 0.5 of the max. intensity of both anodal and cathodal portions. This potential value is substantiated by theoretical considerations and by expl. detns. This potential value of the "half-wave" remained const. and did not depend upon the concn. of the substance forming the polarographic curve. When the metal ion going from the Hg into the electrolyte formed a complex, the potential of the "half-wave" was shifted to more negative values, depending upon the stability of the complex. These anodal studies (conducted by means of the polarograph) were suitable for detecting and for evaluating traces of metals dissolved in Hg, particularly for the base metals. The potential values were dependable even in the presence of large quantities of other electrochem. stable metals.</p> <p>Frank Marash</p>		<p><i>Handwritten: 4</i></p>	
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Polarographic maximum of cadmium amalgam. J. Heyrovský. *Chem. Listy* 56, 267-71 (1962). - There is no difference between the max. on the current-voltage curves of the anodic soln. of Cd amalgam and the max. existing on the cathodic waves. As the former are suppressed by the anions NO_3^- , SO_4^{2-} , Cl^- ; stronger by Br^- , SCN^- ; most efficiently by I^- they have a positive character. The decomposition potential of Cd ions agrees with the electrocapillary zero, i.e. with the potential at which the double layer Hg-soln. is uncharged. The dropping Hg is uncharged during the deposition of Cd, the inhomogeneous electric field does not appear and, according to the Ilkovic theory, the max. cannot exist. The I^- ions cause (by their adsorption on the surface of the polarized Hg) a shifting of the electrocapillary zero toward the more neg. potentials, having no influence on the decomposition potential of the Cd ions. Now the double layer is positively charged. The charging current is formed during each drop and the inhomogeneous field causes a max. on the current-voltage curve. During the anodic max., the potentials are clearly more pos. when the Cd from the Cd amalgam dissolves than in the case of Cd ions. The amalgam is dissolved at more pos. potentials than the electrocapillary zero. The anodic max. is a pos. one and can be suppressed by the adsorptive anions. It explains why the pos. anodic max. is suppressed easily by traces of I^- ions contrarily to the pos. cathodic max. of Cd ions. This is caused by the different direction of the current in these 2 cases. The current supports the adsorption in the case of the anodic max., whereas it disturbs the anions (in the case of pos. cathodic max.) thus disturbing the adsorption. R. Hala

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Polarographic determination of carotene. _____ and P. Hasselbach.
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Oscillographic investigation of the reversibility of processes on the mercury capillary electrodes. J. Heyrovsky. *Chem. Listy* 40, 41 (1946); cf. *C.A.* 41, 542h. An app. was used in which periodic current impulses due to a sine-wave voltage or to a constant voltage alternating in direction charge a polarizable Hg electrode of the dropping or streaming type alternately to neg. and pos. potentials. The potential-time curves are observed on the fluorescent screen of a cathode-ray oscillograph. Depolarizations, involving a single-electron transfer, such as $\text{Fe(III)} \rightarrow \text{Fe(II)}$, $\text{Ce(IV)} \rightarrow \text{Ce(III)}$, $\text{U(VI)} \rightarrow \text{U(V)}$, $\text{Ce(IV)} \rightarrow \text{Ce(III)}$, $\text{Cu(II)} \rightarrow \text{Cu}$, $\text{HClO}_2 \rightarrow \text{HCl}$, or $\text{NO}_2 \rightarrow \text{NO}$.

Na or a 2-electron transfer, such as $\text{Pb(II)} \rightarrow \text{Pb}$, $\text{Sn(II)} \rightarrow \text{Sn}$, or $\text{Cd(II)} \rightarrow \text{Cd}$, show the cathodic and the anodic depolarization kink at the same potential and with the same sym. shape. Such depolarization processes are called "oscillographically reversible." The depolarization from Bi(III) , Sb(III) , In(III) , shown in solns. of SO_4 , NO_3 , ClO_4 , OH , tartrate, or citrate ions, produces the cathodic kink at a more neg. potential than that at which it produces the anodic kink. Such processes are termed "oscillographically irreversible." An addn. of Cl or Br ions to the above solns. changes the irreversible depolarization to a reversible one. The bivalent cations of the transition elements Zn , Cu , Ni , Co , Fe , Mn , and Cr depolarize irreversibly in all solns. in which the electrolytic process involves a 2-electron transfer. From these results it is deduced that the electrolytic acceptance or surrender of more than one electron is not simultaneous but consecutive. The presence of chlorides accelerates the acceptance of electrons by means of an "induction" through deformable Cl ions. The transfer of electrons to or from an inner electron shell of the atom, which is true in the case of the transition elements, is an obvious obstacle to the rate of the electrolytic processes involving 2 electrons, so that such a depolarization proceeds oscillographically irreversibly. Also in *Quart. Revs.* 40, 21 (1946); Heyrovsky.

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cury electrodes. J. Heyrovský (Charles Univ., Prague).
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Retarded electrode reactions. J. Heyrovsky *Chem. Listy* 40, 220-221 (1946). Cases of retarded and normally proceeding electrolytic processes were examined oscillographically and polarographically. On the oscillograph the normal electrode processes cause a sharp V-shaped cut-in in the current-time curve while the retarded processes produce only a shapeless shallow depression extending practically over the half cycle of the applied a.c. Addition of an excess of chlorides changes the shallow depression into a sharp cut-in. The same effect is obtained by heating the solution. Thus there are 2 factors, Cl ions and heat, that promote the rate of the electrode reaction. On the other hand, excess of SO_4 , NO_3 , or ClO_4 ions slows down the electrode reactions as shown by the loss of sharpness of the cut-in of the curve. Also small amts. of ether, phenol, AuCl_3 , or iso-PrOH produce a retarding effect. Such findings show that the electroreduction of O proceeds quickly in acid solutions, slowly in alk. medium, and that nitrobenzene is approx. 4 times more quickly reduced than nitromethane. Ordinary current-voltage curves show smaller diffusion currents in cases of retarded electrode processes than would be expected from the Ilkovic formula. The percentage of the decrease of the diffusion current against the normal one can be calculated from the decrease of the rate of the electrolytic process derived oscillographically. M. Hrudsky

Retarded electrodeposition of metals studied oscillographically with mercury capillary electrodes. J. Heyrovsky (Charles Univ., Prague). *Discussions Faraday Soc.* No. 1, 213-231(1947).—An arrangement was used in which periodic current impulses due to a sine-wave or a rectangular voltage charge a polarizable Hg electrode, of the dropping or streaming type, alternately to neg. and pos. potentials. The potential time curves and derivative curves da/dt are observed on the fluorescent screen of a cathode-ray oscilloscope. A frequency of 50 cycles per sec. was mostly used. In this way the rates of electrodeposition of metallic cations were studied in different electrolytes. Electrodepositions involving single-electron transfers, such as $H^+ = H$, $Na^+ = Na$, $Cu^{2+} = Cu$, $Cu^+ = Cu$, and certain 2 electron transfers such as $Pb^{2+} = Pb$, $Cd^{2+} = Cd$, and $Sr^{2+} = Sr$, show the cathodic and the anodic depolarization kink at the same potential; such processes are termed "oscillographically reversible". The depolarizations due to Al^{3+} , Sn^{4+} , and In^{3+} , shown in solns. of SO_4^{2-} , NO_3^- , ClO_4^- , OH^- , tartrates or citrates, produce the anodic kink at a more pos. potential than that of the cathodic kink. Such electrodepositions are termed "oscillographically irreversible" and are retarded. Addition of Cl and Br ions to these solns. change the irreversible process to a reversible one and increase the rate of deposition. The bivalent ions of the transition elements Cr, Mn, Fe, Co, Ni, Cu, and Zn are deposited irreversibly in all solns. in which the electrode process involves a 2-electron transfer. From the results it is deduced that the electrolytic acceptance of more than one

electron is not simultaneous but consecutive. The second electron is acquired through dismutation, such as $2Zn^+ \rightleftharpoons Zn + Zn^{2+}$, the velocity of which sets the rate of electrodeposition; this is accelerated by heat and by Cl ions and is retarded by films of adsorbed ions. M. F. Querry

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Use of oscillographic potential-time curves in polarography. Proc. Intern. Congr. Pure and Applied Chem. (London) 11, 491-94 (1947) (in English)

Capacity phenomena displayed at mercury capillary electrodes J. Heyrovský, F. Šorm, and J. Forešil (Charles' Univ., Prague, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 12, 11-38 (1947) (In English).

--The capillary electrodes used were the dropping Hg electrode and the streaming Hg electrode. The latter produces a continuously renewed uniform surface of Hg of suitable dimensions because the Hg is forced in a continu-

own stream. A fine jet and upwards through a 4 mm. of soda. For voltammetric studies this has the advantage that complications arising from a growing H₂ drop are eliminated. Results obtained with both capillary electrodes were essentially the same. Studies were made with the polarograph and with a cathode-ray oscillograph. The latter could be connected either to show changes in the pattern of a square wave produced by the phenomena at the capillary electrode directly, or to give only the deriv. of this curve. It was found that certain relatively insol. substances, e.g., pyridine in alkali, butyric acid in acid, and ether in any electrolyte soln., produced a peculiar charging effect by their adsorption on the electrodes. This became apparent as a time-lag on the oscillographic curves or as a diminished condenser current on the polarographic curves which ceased at a characteristic voltage. It was concluded that this phenomenon is caused by a film of the nonelectrolyte adsorbed on the electrode. This film can break up suddenly and can also be rebuilt at speeds greater than 1000/sec.; it has no measurable resistance; it hinders the electrode reduction of Pb⁺⁺, Cd⁺⁺, or nitrobenzene, but does not interfere with that of Ti³⁺. These results are thought to indicate that only one electron is obtained from the electrode by the bivalent ion at any one time and that a subsequent dismutation in soln.: $2Pb^+ \rightarrow Pb + Pb^{++}$ is hindered by the adsorbed film.

Otto H. Müller

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ASH-SLA DETALLURGICAL LITERATURE CLASSIFICATION

The significance of derivative curves in polarography. J. Heyrovský. *Chem. Listy* 43, 149-54(1949).—The deriv. curves first used in polarography were the oscillographic (dV/dt) - t curves showing the dependence of the differential quotient of the voltage (dV/dt) with respect to the time, t . They are used for analytical purposes and for the study of the rate of depolarization processes. Analogous diagrams showing the dependence of dI/dE on E where 2 equal dropping electrodes are polarized. The difference between them, dE , being applied from a potentiometric bridge. The advantage of the polarographic derivative ($dI/dE - E$) curve over the ordinary "primitive" current-voltage, $I - E$, curve are: at the half-wave potential the deriv. curve shows a max. the summit of which gives by its abscissa the quantity (half-wave potential), and by the ordinate the quantity (a fraction of the diffusion current). The curve returns to zero at any diffusion current so that traces of the less-noble constituents are determinable in a large excess of the nobler ones. Complex waves composed of 2 or more elements. Coinciding waves are resolved by the deriv. into the components. Maxima of the deriv. curves due to the inflection point at the half-wave are well developed also when the primitive diffusion currents are indistinct. The deriv. maxima are on the whole more conspicuous than the

waves of the primitive curves even when the depolarizers are greatly dil. The deriv. of the current-voltage curves with only one dropping electrode can be obtained: (1) by use of a condenser and galvanometer parallel to a resistance through which the electrolytic current flows; (2) by use of one galvanometer with 2 coils one of which indicates the current passing through it while in the other the deriv. dI/dE is induced, which is shown by a second galvanometer; (3) by leading the primitive current into an induction coil which induces the derivative dI/dE in the secondary coil. In the last 3 cases, the increase of the applied e.m.f., E , is supposed to be strictly proportional to the time so that $dE = Kdt$. The oscillographic (dV/dt) - V diagrams are analogous to ordinary polarograms yet show very minute differences between organic isomers such as *o*-, *m*-, *p*-nitrophenols, nicotine, proline, and isonitrotoluene acids and nitrobenzene and *o*-, *m*-, and *p*-nitrotoluenes. I. Heyrovský

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279-85 (in English).

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Polarization effects of surface films at the dropping and streaming mercury electrodes. _____ and M. Matyas. Coll. Czech. Chem. Commun. 16, 455-64 (1951) (in English)

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PHASE I BOOK EXPLOITATION

CZECH/2433

International Polarographic Congress. 1st, Prague, 1951

Sborník I. Mezinárodního polarografického sjezdu. Díl 3: Hlavní referáty přednesené na sjezdu. Proceedings...Vol 3: Reviews Read at the Congress. Praha, Přírodovědecké vyd-ví [1952] 774 p. 2,000 copies printed.

Resp. Ed.: Jiří Koryta, Doctor; Chief Ed. of Publishing House: Milan Skalník, Doctor; Tech. Ed.: Oldřich Dunka.

PURPOSE: The book is intended for chemists, chemical engineers, and physicists.

COVERAGE: The book is a collection of reviews and original papers read at the International Polarographic Congress held in Prague in 1951. Uses of polarography in organic and inorganic analysis, biochemistry, medicine, and industrial chemistry are discussed. In the section, Reviews Read at the Congress, Russian and either German or English translations of each review are presented. In the section, Original Papers Read at the Congress, only those translations in Russian, German, and English which

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Proceedings (Cont.)

CZECH/2433

have not been published in Volume I are presented. The following scientists participated in the opening of the Congress: Professor Wiltor Kemula, Dean of the Faculty of Sciences, Warsaw; Doctor Jaromir Dolansky, Minister of Planning; Professor Jaroslav Herovsky, Chairmen of the Congress; and Professor Jaroslav Fukatko, Chairman of the Center for Scientific Research and Technical Development. References follow each paper.

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